Flavor of Browning Reaction Products

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    With the exception of fresh vegetables and fruits, most
consumed food has   to be subjected to processing (boiling,
broiling, roasting, canning, baking, concentration, pasteuriza-
tion,...etc.) to render it edible; to increase its consumer
acceptance or to extend its shelf life. Table I lists the
consumption of food commodities per capita in the United
States (1). About 78% of these comodities are processed, and
account for approximately 75% of the American family food budget.
    Natural food flavors such as terpenes, hydrocarbons,
alcohols, aldehydes, ketones, esters, acids, lactones, amines,
sulfur compounds are enzymatically produced in fruits and
vegetables. On the contrary, processed food develops its
characteristic acceptable flavors from chemical reactions within
its components at temperatures far below those at which its major
components, i.e., lipids, proteins and carbohydrates pyrolyze.
Food flavor precursors responsible for the productivity of
volatile flavors are given in Table II.
    Aqueous flavor precursors undergo nonenzymic browning during
processing, which is the most important flavor producing reaction.
Also, at low temperature pyrolysis, i.e., roasting between
$100-270°C$, these compounds undergo thermal degradation, producing
new compounds some of which have desirable organoleptic notes.
Some degradation products react further. For example, all purines
are decomposed upon heating in acid media at temperatures above
$100°C$ to glycine, formic acid, carbon dioxide and ammonia.
Methylated purines give rise to methylamine instead of ammonia.
    Proteins and glycoproteins participate in the browning
reaction via their free-NH_2 groups. Furthermore, during proces-
sing, compounds of these two classes undergo hydrolysis and
degradation;thus ammonia, hydrogen sulfide, peptides, amino acids,
amines and sugars are produced. A delicious taste peptide which
has the following structure: H-Lys-Glc-Asp-Glu-Ser-Leu-Ala-OH was
isolated from beef gravy (2). In animal cells, the widely occur-
ring peptides are carnosine, anserine, glutathione, phosphopep-
tides, lipopeptides and nucleopeptides. The largest class of

Table I

Consumption of Major Food Commodities Per Capita in USA, lb

Commodity	1960	1970	1974	1975	1976	1977
Meats:						
Beef	134.1	151.4	152.5	145.4	155.3	154.8
Veal	64.3	84.1	86.4	88.9	95.7	93.2
Lamb and mutton	5.2	2.4	1.9	3.5	3.3	3.2
Pork (excluding lard)	4.3	2.9	2.0	1.8	1.7	1.5
Fish (edibly weight)	60.3	62.0	62.2	51.2	56.4	56.9
Poultry products:	10.3	11.8	12.2	12.2	12.9	12.8
Eggs	42.4	39.5	36.6	35.4	34.9	34.5
Chicken (ready-to-cook)	27.8	40.5	41.1	40.3	43.3	44.3
Turkey (ready-to-cook)	6.2	8.0	8.9	8.6	9.2	9.2
Dairy products:						
Cheese	8.3	11.5	14.6	14.5	15.9	16.3
Condensed and evaporated milk	13.7	7.1	5.6	5.0	4.7	4.4
Fluid milk and cream (prod.weight)	321.0	296.0	288.0	291.1	292.0	289.4
Ice cream (product weight)	18.3	17.7	17.5	18.7	18.1	17.7
Fats and oils-total, fat content	45.3	53.0	53.2	53.3	56.1	54.4
Butter (actual weight)	7.5	5.3	4.6	4.8	4.4	4.4
Margarine (actual weight)	9.4	11.0	11.3	11.2	12.2	11.6
Lard	7.6	4.7	3.2	4.0	3.6	3.5
Shortening	12.6	17.3	17.0	17.3	18.1	17.5
Other edible fats and oils	11.5	18.2	20.3	20.3	22.0	21.6
Fruits:						
Fresh	90.0	79.1	76.3	81.3	83.6	82.4
Citrus	32.5	27.9	26.8	28.7	28.6	25.2
Noncitrus	57.5	51.2	49.5	52.6	55.0	57.2

Table I (cont'd)

Consumption of Major Food Commodities Per Capita in USA, lb

Commodity	1960	1970	1974	1975	1976	1977
Processed:						
Canned fruit	22.6	23.3	19.6	19.3	19.2	19.5
Canned juice	13.0	14.6	14.7	15.3	15.3	13.7
Frozen (including juices)	9.1	9.8	11.3	12.6	12.2	12.4
Chilled citrus juices	2.1	4.7	5.2	5.7	6.2	5.8
Dried	3.1	2.7	2.5	3.0	2.7	2.6
Vegetables:						
Fresh	96.0	91.0	93.6	93.9	94.5	93.1
Canned, excluding potatoes and sweet potatoes	43.4	51.2	53.3	52.1	52.8	52.8
Frozen, excluding potatoes	7.0	9.6	10.2	9.7	10.2	9.7
Potatoes, (including fresh equivalent of processed)	105.0	115.3	112.3	120.2	114.7	120.7
Sweetpotatoes, (Including fresh equivalent of processed)	6.5	5.2	5.1	5.3	5.3	5.0
Grains:						
Wheat flour	118	110	106	107	111	107
Rice	6.1	6.7	7.6	7.7	7.2	7.8
Other:						
Coffee	11.6	10.5	9.5	9.0	9.4	6.9
Tea	0.6	0.7	0.8	0.8	0.8	.9
Cocoa	2.9	3.1	3.0	2.6	3.0	2.7
Peanuts (shelled)	4.9	5.9	6.4	6.5	6.3	6.5
Dry edible beans	7.3	5.9	6.7	6.5	6.3	6.0
Melons	23.2	21.2	17.2	17.5	18.6	19.0
Sugar (refined)	97.4	101.8	96.6	90.2	94.7	95.7

Reference (1)

Table II

Food Flavor Precursors and Their Flavor Components

Precursors		Possible Flavor Components Produced	
Class	Number	Per Compound	Per Class
a- Aqueous Flavor Precursors			
1- Glycoproteins			
2- Glycopeptides			
3- Proteins			
4- Peptides	60	40	2,400
5- Amino Acids	)		
6- Amines	} 35	40	1,400
7- Nucleotides	)		
8- Nucleotide sugars	}		
9- Nucleotide sugaramine	} 35	40	1,400
10- Nucleotide acetylsugaramine	)		
11- Peptide bound nucleotide	12	40	480
12- Nucleosides	12	40	480
13- Purines and pyrimidines	12	25	300
14- Sugars	)		
15- Sugaramine	} 50	50	2,500
16- Sugar phosphate	)		
17- Organic acids	25		
Subtotal	>241	>275	>8,960
b- Non-Auqeous Flavor Precursors			
1- Neutral lipids	25	50	1,250
2- Polar Lipids	25	50	1,250
3- Isoprenoids	150	5	750
4- Carotenoids	10	25	250
5- Unsaponifiable compounds			
Subtotal	>210		>3,500
22 Grand total	>451		>12,460

peptides in plants consist of γ-glutamyl dipeptides along with some tripeptides, one of which is homoglutathione (γ-glutamylcysteinyl-β-alanine) which replaces glutathione in some enzymic reactions (3). About thirty-five amino acids and amines occur naturally in foods. D-ribose is found in nucleotides, D-ribulose, D-lyxose, D-xylulose, glucose, fructose, sedoheptulose, and glyceraldehyde are present as phosphoric acid esters in the products of carbohydrate metabolism. Fucose is a constitutent of blood group substances which contain galactose and mannose. The presence of carbohydrate alcohols in vegetables, fruits and animals may be accounted for by a reduction of the reducing sugars, or through decarboxylation of the corresponding higher aldonic acids. Sorbose, glucose, sucrose, inositol, mannitol, pentitol and two unidentified sugars were reported in cocoa beans (4).

Sugar acids, mono-, di-, and tri-carboxylic acids, keto-, hydroxy-acids as well as unsaturated organic acids are present in foods. While uronic acids participate in the browning reaction, others might accelerate or retard the reaction.

Non-aqueous flavor precursors contribute directly and indirectly to food flavors. Boar meat lipids contain 5-androst-16-ene-3-one which is responsible for noticeable undesirable notes (5). The characteristic flavors of mutton and goat meat are attributed to the presence of odd-numbered n-fatty acids, and abnormal proportion of branched chain fatty acids (6). During processing of foods, lipids undergo autoxidation, hydrolysis, dehydration, decarboxyltion, and degradation. Thermal degradation of neutral lipids, polar lipids and free fatty acids produce the following classes of compounds (7-13)   :-(1)n- and iso-alkanals, (2) alkadianals, (3) oxo-alkanals, (4) alkenals, (5) alkadienals, (6) aromatic aldehydes, (7) methyl ketones, (8) saturated and unsaturated alcohols, (9) γ- and δ- lactones, (10) hydrocarbons, (11) keto- and hydroxy-acids, (12) dicarboxylic acids, and (13) saturated and unsaturated fatty acids, containing less carbon atoms than the parent ones.

Lipids in foods vary from traces as in cereals to 30-50% as in nuts. The physical state and distribution of lipids vary considerably among food items. In each item lipid distributions affect its flavor as it undergoes chemical reactions and act as a flavor components vehicle or partitioning medium. Furthermore, lipids have a pronounced effect upon the structure of food items. Fatty acids of neutral (triglycerides) and polar lipids of beef and pork are tabulated in Table III.

Pork fat contains more unsaturated fatty acids than beef and its linoleic acid content is double that in beef. Heat produced volatiles in red meat fats are listed in Table IV. The presence of pyrazines in the volatiles of beef fat is due to the presence of nitrogenous compounds in the fat amounting to 0.1-0.2%N, (Kjeldhal method). These compounds might be proteins, peptides, amino acids, and amine moities in polar lipids. Such compounds

Table III

Fatty Acids Composition of Beef and Pork Lipids

| Fatty Acids | Triglcerides | | Polar Lipids | |
| | Beef | Pork | Beef | Pork |
	% of Total Fatty Acid Content			
a.- Saturated				
Capric	0.1	0.1	–	–
Lauric	0.1	0.2	–	–
Myristic	2.2	1.2	2.6	2.0
Palmitic	27.5	23.9	13.2	20.0
Stearic	16.9	11.6	15.6	11.0
Total	46.8	37.0	31.4	33.0
b.- Monounsaturated				
Tetradecenoic	1.0	–	0.9	0.2
Palmitoleic	4.7	7.4	2.2	2.3
Oleic	41.3	45.3	21.2	16.2
Total	47.0	52.6	24.3	18.8
c.- Dienoic				
Tetradecenoic	0.6	–	1.3	0.6
Linoleic	4.4	8.7	20.2	27.9
Docasadienoic	–	–	–	0.9
Total	5.0	8.7	21.5	29.3
d.- Trienoic				
Linolenic	1.1	1.6	1.8	1.0
Eicosatrienoic	–	–	1.9	1.6
Total	1.1	1.6	3.7	2.6
e.- Tetraenoic				
Arachidonic	0.1	0.1	19.1	16.3
Total	0.1	0.1	19.1	16.3

Reference (14)

Table IV
Heat Produced Carbonyls In Red Meat Fats

Volatile Compounds	Pork	Beef	Lamb
ALKANALS			
Ethanal (Acetaldehyde)	10	9a,10	
n-Propanal	10	9a,10	
n-Pentanal	7	8	
n-Hexanal	7,10	8,9,10	10
n-Heptanal	7	8,9	
n-Octanal	7,10	8,9	
n-Nonanal	7,10	8,9	10
n-Decanal	7	8,9	
n-Undecanal	7		
n-Dodecanal	7		
METHYL-ALKANALS			
Methylpropanal		9a	
Methylbutanal	7	8,9a	
ALKANEDIAL			
Ethanedial (Glyoxal)		9a	
OXOALKANAL			
2-Oxopropanal (Pyruvaldehyde)		9a	
2-ALKENAL			
2t-Butenal (Crotonal)		9a	
2t-Heptenal	7	8,9	
2t-Octenal	7,10	8,9	
2t-Nonenal	7,10	8,9	10
2t-Decenal	7,10	8,9	10
2t-Undecenal	10	8	10
2,4-Alkadienal			
2,4-Heptadienal	10		
2,4-Nonadienal	10		
2,4-Decadienal	10	8,10	
2-ALKANONE			
Acetone		10	
2-Butanone		9a	
2-Decanone	7	7	
2-Undecanone		7	
2-Tridecanone		8	
2-Pentadecanone		8	
2-Heptadecanone		8	

Table IV (cont'd)

Heat Produced Carbonyls in Red Meat Fats

Volatile Compounds	Pork	Beef	Lamb
HYDROXY-2-ALKANONE			
3-Hydroxy-2-butanone(acetoin)		9a	
PYRAZINE			
2,5-Dimethyl-		8	
2-Ethyl-		8	
2-Ethyl-3,6-dimethyl-		8	
2-Ethyl-5-methyl-		8	
2,3,5-Trimethyl-		8	

Reference (7,8,9,10)
"a" designates heating in nitrogen atmosphere, otherwise in air.

degrade during heating and produce ammonia and basic compounds. When ammonia, amino acids and degraded nitrogenous compounds react with α-dicarbonyls produced from lipid oxidation, pyrazines are formed.

Cooked chicken flavor concentrate (13) contained the following aldehydes; 3c-nonenal; 4c-decenal; 2t,4c-decatrienal; 2t,5c-undecadienal; 2t-dodecenal; 2t,4c-docadienal; 2t,6c- and 2t,6t-dodecadienal 2t-tridecenal; 2t,4c-tridecandienal; 2t,4c,7c-tridecatrienal; and 2t,4c-tetradecadienal. Three of these aldehydes: 4c-decenal; 2t,6c-dodecadienal; and 2t,4c,7c-tridecatrienal are typical breakdown of arachidonic acid, and to a major extent also 2t,5c-undecadienal. These aldehydes play an important role in cooked chicken flavor via the browning reaction. 2,4-Decadienal which is considered to be a key compound of chicken aroma, was found in the volatiles of cooked chicken (15,16). 2,4-Heptadienal; 2,4-nonadienal and 2,4-decadienal were identified in heated pork fat (10) and heated beef fat (8,10). Dicarbonyls, dienals, trienals undergo amino-carbonyl reactions, resulting probably in the formation of meaty flavor notes in specific proportions characteristic of each species. Although their yield is small in comparison with monocarbonyls, their high reactivities are responsible for thier important role in flavor production.

The complexity of food flavor precursors is manifested by the number of compounds estimated in each class of compounds and by the possible total number in a single raw food. The possible number of flavor components produced per one compound of flavor precursor is estimated in the range 10-150, but is reduced to 5-40 to eliminate compounds that might be produced

by more than one precursor and to account for variations in
processing methods. One hundred compounds were identified in
thermal degradation products of glucose (17,18,19): aldehydes
ketones, aromatics, furans, oxygenated furans, non-volatiles.
Sugars react with ammonia at temperatures ranging from 20 to
260°C., to produce heterocyclic compounds : substituted imidazoles,
substituted pyrazines, substituted piperazines, pyridine and
substituted pyridines(20). At 0-120°C., α-dicarbonyls
(2,3-butadione, ethanedial "glyoxal", 2-oxopropanal
"pyruvaldehyde", and α-hydroxycarbonyl "glycolaldehyde" react
with ammonia in presence of formaldehyde to give substituted
imidazoles. Dipeptides react with sugars either as an entity
or as amino acids produced by hydrolysis during processing. In
the first case, one compound is formed, pyrazinone (21), in the
second case numerous flavor compounds are produced from the
reaction of the two amino acids with sugar. The reactivity of
dipeptides towards reaction with carbonyl compounds is much
higher than that of amino acids. The taste of glycyl-L-leucine
is very bitter, the product of its reaction with glyoxal has an
astringent, a little sour and later a mild taste. Some products
from the browning reaction and pyrolysis of flavor precursors
react with ammonia and hydrogen sulfide, thus increasing the
number of flavor components produced from food precursors. The
molecular structure of the amino acid influences the flavor notes
in the food. For example, thiophenes are reported in the vola-
tiles produced from the pyrolysis of cysteine or from its
reaction with glucose or pyruvaldehyde (22,24) but were absent
in the case of cystine (23,24).

Hundreds of compounds have been identified in the volatile
flavor components of processed foods. Hydrocarbons, alcohols,
ethers, aldehydes, ketones, acids, acid anhydrides, esters,
aromatic, lactones, pyrones, furans, pyridines, pyrroles,
n-alkylpyrrole-2-aldehydes, pyrazines, sulfides, disulfides,
thiols, thiophenes, thiazoles, trithiolanes, thialdine ...etc.
Each compound has a characteristic note and a specific threshold
which makes its contribution to food flavor unique. But none of
the individual compounds were reported to completely produce the
characteristic flavor of the processed food. This indicates that
the food flavors are of mixed flavor notes of numerous compounds,
while others are necessary for its synergistic effect, others
exert a background of modifying effect.

Browning reaction has become a major topic of food research
because of its relevance to the desirable and undesirable changes
(flavor, color, texture, and nutritive value) occurring in foods
during processing and storage. During the Second World War and its
post era, research on food deterioration due to nonenzymic
browning received considerable attention due to the problems
resulting from the necessity to prepare dehydrated foods and
food concentrates which had to be stored under tropical conditions
without serious deterioration.

The purpose of this paper is to review the numerous papers published on flavors, tastes and odors resulting from the browning reaction. Investigations of model systems which have been observed under laboratory conditions are considered and their possible significance in basic and industrial processes will be discussed. Speculation on the possible correlation between model system results and specific processed food items will be presented. Results of recent work in our laboratory on flavor notes developed upon heating ribose with various amino acids will be discussed.

The numerous purely chemical papers are considered to be outside the scope of this paper. The reader is referred to several reviews on the subject (25-30). Comprehensive reviews on nonenzymic browning in relation to specific food problems had been published (31,32,33).

As flavor production in natural food is governed by too complicated reactions due to its complex components (Table II), chemists concentrated their research efforts on simpler systems to understand the reactions involved and their products.

Amino Acids-Sugars Model Systems

Model system studies of the reaction between single amino acids and naturally occurring substances capable of reacting with them has furnished valuable information leading toward an understanding of food flavors. The well known Strecker degradation of α-amino acids, Schonberg and Moubacher (25), has been used as the central reaction around which other amino compound degradation systems may be oriented. In this reaction α-amino acids are deaminated and decarboxylated by specific carbonyl compounds or others to yield aldehydes and ketones containing one carbon atom less. β-amino acids also undergo oxidative deamination and decarboxylation to a ketone with one less carbon atom; e.g., β-amino-n-butyric acid produces 2-propanone, which also results from the Strecker degradation of α-amino-isobutyric acid. Organic di- and tricarbonyls are not the only oxidants effective in Strecker degradations. Hydrogen peroxide in presence of ferrous sulfate degrade α-amino acids at room temperature; for example glycine yields formaldehyde. The co-oxidation of sulfur-containing amino acids in an auto-oxidizing lipid system indicates that lipid peroxides act as oxidants (34). The resulting carbonyl compounds from amino acids through Strecker degradation participate in the formation of desirable characteristic flavors during processing or undesirable ones responsible for flavor deterioration during storage.

Flavors and odors given by amino acids and sugars in dilute aqueous solutions at different temperatures has been the subject of intensive studies by various researchers. Tables V and VI summarize the descriptive aroma evolved from reacting carbonyl compounds with amino acids at 100, and 120/180°C., respectively

Table V

Aromas Developed by the Reactions of Carbonyl Compounds and Various Amino Compounds at 100°C

Amino Compounds	Dihydroxyacetone	Glucose	Fructose	Maltose	Sucrose
Glycine	baked potato(35)	caramelized sugar (36,39), faint beer(40).	unpleasant carmel smell(36).	weak(36)	objectionable weak NH₃(36)
α-Alanine	weak caramel(35)	beer aroma(40)			
Valine	strong,yeasty protein hydrolyzate(35)	rye bread(37) fruity,aromatic (39)	---		---
α-Aminobutyric	---	maple(38)	---	---	---
Leucine	strong,cheesy,	sweet chocolate(37), toast(39),bread(40) rye bread(38)	---	---	---
Isoleucine	moderate crust (35)	musty(37),fruity, aromatic(39)	---	---	---
Serine	vaguely bread-like(35)	maple syrup(38)	---	---	---
Threonine	very weak(35)	chocolate(37) maple(38)	---	---	---
Phenylglycine	---	bitter almond(38)			
Methionine	baked potato(35)	overcooked sweet potato(36) potato(37)	objectionable chopped cabbage(36)	overcooked cabbage(36)	unpleasant burned wood(36)

Table **V** (cont'd)

Aromas Developed by the Reactions of Carbonyl Compounds
and Various Amino Compounds at 100°C

Amino Compounds	Dihydroxyacetone	Glucose	Fructose	Maltose	Sucrose
Cysteine	mercaptan, H_2S (35)	meat(39) sulfide (37)	---	---	---
Cystine	---	meat, burnt turkey skin(39)	---	---	---
Proline	very strong cracker,crust, toast(35)	corn-like(39) burnt protein (37)	---	---	---
Hydroxyproline	weak, vaguely like proline(35)	potato(39)	---	---	---
Arginine	very weak(35)	popcorn(37) butterscotch(39)	---	---	---
Histidine	very weak(35)	buttery note(39), none(37)	---	---	---
Glutamine	---	chocolate(37)	---	---	---
Methylamine	---	empyreumatic taste(40)	---	---	---
Ammonia	---	tarry odor, bitter taste(40)	---	---	---
Phenylalanine	very strong, hyacinth(35)	rancid caramel, unpleasant(36) violets(37) rose perfume(39)	stinging smell, very objectionable(36)	pleasant sweet caramel(36)	unpleasant sweet caramel(36)

Table V (cont'd)

Aromas Developed by the Reactions of Carbonyl Compounds ans Various Amino Compounds at 100°C

Amino Compounds	Dihydroxyacetone	Glucose	Fructose	Maltose	Sucrose
Tyrosine	--	caramel(37)	--	--	--
Aspartic	very weak(35)	rock candy(37)	--	--	--
Glutamic	chicken broth(35)	oldwood pleasant(36)	too weak(36)	too weak(36)	pleasant caramel(36)
Arginine	--	buttery note(39)	--	--	--
Lysine	strong dark corn syrup(35)	baked sweet potato(36)	objectionable fried butter (36)	unpleasant wet wood (36)	rotten wet potato(36
α-Methylamino-butyric	--	maple(38)	--	--	--
α-Amino-isobutyric	--	maple(38)	--	--	--

References (35,40)

Table VI

Aromas Developed by Heating Glucose with Various Amino Acids at 120°C and 180°C

Amino Acid	Aroma Description 120°C	180°C	Amino Acid	Aroma Description 120°C	180°C
Valine	moderate breadcrust(41)	penetrating chocolate(37)	Lysine	weak(41)	bread-like(37)
Leucine	moderate breadcrust(41)	burnt cheese(37)	Methionine	strong baked potato(41)	potato(37)
Isoleucine	moderate breadcrust(41)	objectionable burnt cheese(37)	Proline	strong bread-crust cracker (41)	pleasant bakery aroma(37)
Threonine	weak(41)	burnt(37)	Histidine	no significant aroma(41)	cornbread(37) buttery note(38) butterscotch(37)
Phenylalanine	strong flower (41)	violets,lilac (41)	Glutamine		
Aspartic	strong breadcrust(41)	caramel(37)	Tryptophan	strong(41)	
Glutamic	moderate(41)	brunt sugar(37)			
Arginine	no significant aroma(41)	brunt sugar(37)			

References (37,38,41)

(35-41). The aroma produced by the interaction of sugars and
amino acids ranged from pleasant to objectionable. The molecular
structure of sugar influences the resulting aroma of the products
of its reaction with the amino acid. While a pleasant caramel
sweet aroma developed upon reacting phenylalanine with maltose,
an unpleasant caramel aroma developed with fructose, and a
hyacinth aroma in case of dihydroxyacetone. While the aroma of
methionine-sugar browning product was reminiscent of a pleasant
baked potato in presence of dihydroxyacetone, aroma notes of
overcooked potatoes developed with glucose. In presence of a
reducing disaccharide (maltose), overcooked cabbage aroma was
noticed and an unpleasant burnt wood aroma developed in presence
of non-reducing disaccharide (sucrose). Proline, valine and
isoleucine in presence of glucose gave a pleasant bakery
aroma (41). Keeney and Day (42) studied the character odor of
the products of Strecker Degradation of amino acids using isatin
as the oxidant (Table VII).

Table VII

Aroma of Strecker Degradation Products of α-Amino Acids
with Isatin (Diketodihydroindole)

Amino Acids	Aldehyde	Sensory Description	
		Keeney & Day (42)	Others (43,44)
α-Alanine	acetaldehyde	malty	reminiscent of wine, coffee (43)
Valine	2-methyl- propanal	apple	fruity, banana-like (43) green, pungent sweet (44)
Leucine	3-methyl- butanal	malty	fruity, peach-like (43) burnt, green, sickly (44)
Isoleucine	2-methyl- butanal	malty-apple	burnt, sickly (44)
Norleucine	pentanal	flower	slightly fruity, herb- aceous, nut-like (43) burnt-green (44)
Phenyl- alanine	phenylacet- aldehyde	violets	hyacinth odor, resemble benzaldehyde in taste (43)
Glutamic		bacterial agar	
Cystine	methional	cheesy-brothy	

References (42,43,44)

There is some agreement and disagreement between the sensory notes
stated in Tables V and VII, which may be attributed to variations
in the concentration of the reactants and lack of agreement on
description of sensory notes. The discrepancies can be resolved,
by a careful consideration of the specific conditions of the
reaction. It is possible that both the nature and extent of the

reaction vary widely with the principal variables
(concentration, temperature, heating period, specific reactants).
Unfortunately, many of the papers insufficiently define the
experimental conditions for an adequate evaluation of the
results. The description of odor and taste notes of a product
or a compound varies according to its concentration, the media
used for evaluation(water, paraffin oil, skim milk...etc), and
the sensory evaluator.

The data in Table VI indicate that the aromas developed
when sugars and amino acids were heating at 120 and 180°C, were
quite different from those produced at 100°C. Noticeable
differences exist between aroma notes developed at 120°C and
180°C, this may be attributed to sugar degradation notes which
become noticeable in the system heated at 135°C and above.

All aliphatic compounds containing primary or secondary
amine group react in browning reaction but at different rates
depending upon the molecular structure. The reactivity of the
reactants (amino acids, carbonyl compounds) in the browning
reaction had been reported in the literature as:

a. intensity of color developed,

b. amount of carbonyl compounds determined by GC or
as dinitrophenylhydrazones.

c. percent loss of reactants (one reactant or both).
It is very hard to compare results reported in the literature,
as there are various variables influencing the data. Concentra-
tion of reactants, ratio of amine compound to sugar or carbonyl,
reaction in buffer or water, molarity and type of buffer used,
pH of buffer, duration of reaction. Rate of carbonyl compounds
formation will be the criterion used for reactivity except
in few occasions where the percent loss of one of the reactants
or both will be referred to in the manuscript.

Rooney et al (45) reported that the rate of carbonyl
formation varied with the molecular structure of sugar. Xylose
was most reactive as it produced the greatest quantity of
carbonyls, followed by glucose, then maltose. In the presence
of these sugars isoleucine was more reactive than phenylalanine.
In a study on the Strecker degradation of valine-carbonyl,
diacetyl showed the greatest reactivity followed by sorbose>
arabinose>xylose>fructose>glucose>sucrose>rhamnose, Self(46).
The number of volatile carbonyls produced by the reaction of
glucose and glutamic at pH 5.0,6.5 and 8.0 at 100°C was almost
equal. When these systems were heated at 180°C, the number of
volatiles was greater and increased more drastically as pH
increased to alkalinity (36). The amount of aldehydes produced
from mixtures of 0.01M amino acid and 0.1M glucose in water was
far below those produced in 0.01M phosphate buffer at pH6.5,
which in turn was far below the amount obtained at pH 7.5. The
addition of phosphate buffer increased the amount of aldehydes
produced signigicantly. The amount of aldehyde produced is also
influenced by the chain length of the acid. In general,

straingt chain amino acids produced more aldehydes than branched chain amino acids of the same number of carbon atoms (46).

Alanine, valine, serine, glutamic, glutamine, methionine, taurine, histidine, creatine, citrulline, carnosine, cystine, systeine, aspartic, asparagine, leucine, isoleucine, tyrosine, phenylalinine, tryptophan, α-aminobutyric, proline, ornithine, 2-pyrrolidone-5-carboxylic, threonine, glycine, lysine, arginine, cysteine were identified in aqueous red meat flavor precursors (47). Ribose was also reported as the major sugar. Flavor evaluation of the browning reaction products of these amino acids and ribose were undertaken. 0.1M solution of each amino acid was prepared by dissolving the amino acid in 0.05M Sørensen phosphate buffer and readjusting the pH by the addition of monopotassium or dipotassium phosphate. 0.1M ribose solution was prepared in the same buffer. Ten ml of amino acid and 10ml of ribose solutions were pipetted in 50ml glass ampoule and 50ml round bottom flask with 24/40 glass joint. 1.0 mMoles of insoluble amino acids were weighed directly in reaction vessels, and 10ml buffer added. To study the effect of heating on flavor of amino acids in absence of ribose, 10ml buffer were pipetted in glass ampoules and flasks along with the amino acid. The ampoules were sealed after evacuation, and heated for one hour at 180°C. The flasks were heated in glycerol bath at 100°C, after fitting with condensors. After the heating period, the flasks and the ampoules were removed, cooled in wet ice, and the contents transferred to vials and kept at -10°C. All experiments were run in triplicates. In absence of ribose, while sulfur containing amino acids solutions produced sulfury notes upon heating, none of the others developed any flavor notes. Table VIII lists the striking flavor notes produced by heating various amino acids-ribose solutions at 100° and 180°C.

Table VIII

Flavor Notes Produced by Heating Amino Acid-Ribose
AT 100°C and 180°C

| Amino Acid | Flavor Description | |
	100°C	180°C
Alanine	very mild caramel	sweet burnt caramelized sugar
Valine	sickly sweet	penetrating burnt chocolate
Serine	sweet bouillion	burnt sugar
Glutamic	brothy, slightly sweet, lingering in mouth	roasted meat
Methionine	sulfury, savory	crust of roast meat
Cysteine	sulfury, rotten egg	sulfury, spicy meat
Taurine	pleasant toffee	sickly, sweet, burnt caramel

Table VIII (cont'd)

Flavor Notes Produced by Heating Amino Acid-Ribose
At 100°C and 180°C

| Amino Acid | Flavor Description | |
	100°C	180°C
Tryptophan	oily aromatic, sugar sweet	oily aromatic, naphththalene
Phenylalanine	sharp flower	flowery with aromatic and caramel notes, undersirable
Histidine	salty, slightly bitter caramelized toffee	pleasant slightly burnt caramel
Creatine	slightly salty	slightly sweet caramel
Tyrosine	slight caramel	custard slightly burnt sugar
Leucine	bitter almond	toasted bread
Aspartic	bread crumb	caramelized bread crust
Cystine	hard boiled egg yolk	meaty with H_2S note
Glutamine	caramel with burnt sugar note	butterscotch
Asparagine	desirable burnt sugar	creamy butterscotch sugar
α-Aminobutyric	undersirable burnt sugar	maple
γ-Aminobuturic	burnt sugar	maple
β-Aminobutyric	custard	maple
Arginine	burnt sugar	buttery, burnt sugar
Ornithine	bread crumb	bread-like
Proline	bread crumb	cracker, toast
Cysteic	undersirable, sulfury	meaty, sulfury
2-Pyrrolidone -5-carboxylic	brothy	meaty, pleasant
Isoleucine	aromatic, undesirable	burnt cheese
Glycine	caramel, faint	burnt sugar
Lysine	custard	bread
Homocystine	canned milk	scorched boiled milk
Threonine	custard weak	burnt custard
Citrulline	toffee-like	meaty
Carnosine	buttery-toffee	meaty

The previous discussion covered Strecker degradation of amino acids sugar aqueous solutions. A limited number of investigations were carried out on the nature of the browning reaction at high temperature, i.e. low temperature pyrolysis and at low moisture content. Rohan and coworkers had provided an extensive research on model systems simulating cocoa nib roasting in absence of lipid. Amino acids and sugars were responsible for chocolate flavor development (48,49,50,51). While the degradation of amino acids in cocoa beans during roasting was incomplete, the degrading agent, reducing sugar was completely destroyed.

In a study on model systems prepared from single amino acid and glucose in molar ratio 2:1, approximating the composition of shell-free cocoa beans, Rohan and Stewart (52) reported that amino acid destruction from heating was temperature dependent and practically ceased after one hour. Sugar destruction contintued at a rate dependent on reaction temperature until the end of the experiment (Table IX).

Table IX

Destruction of Amino Acids and Peducing Sugars on Heating
Chocolate Aroma Precursor Extract

| Heating | | | Destruction Percent | | |
°C	Min.	Amino Acids	Red. Sugars	Total Sugars	Aroma
50	30	6.2			
50	60	8.9	27.0		
50	120	8.9	41.1		
100	30	18.8	27.5	35.8	Cocoa
100	60	29.6	56.6	79.6	Cocoa
100	120	30.9	81.4	22.8	Cocoa
120	30	43.0	84.1	38.9	Cocoa
120	60	54.4	100	79.2	Cocoa
120	120	54.4	93.5	91.2	Cocoa
150	10	58.8			Cocoa
150	30	81.7			Cocoa
150	60	85.4			
150	120	85.1			

Reference (52)

The failure of amino acid degradation to go to completion and the relation between maximal destruction and temperature might be attributed to the fact that individual amino acids reacted at different rates at different temperatures. For example certain amino acids, leucine, arginine, methionine, and lysine showed little or no detectable reaction at 100°C after one hour, while others were reactive at this temperature(Table X). At higher temperatures, rate of amino acid degradation was measurable and proportional to the temperature of the reaction.

The effect of increasing temperature on the amount of amino
acid destroyed in one hour was noticeably greater at temperatures
above 140°C than below 120°C. Between 120° and 140°C.,increase
in reaction temperature had less marked effect on the reaction
due to changes in the physical condition of the reaction mixture.
At about 150°C. glucose melts and , as it might be expected, its
mixture with amino acids would begin to melt at lower temperature.

Table X

Destruction of Amino Acids After Heating With Glucose at
Different Temperatures for One Hour

Temp. °C	Destruction Percent								
	Al	PhAl	Threo	Glu	Meth	Leu	Val	Arg	Lys
80					0.9		7.0		
90		13.9	2.0	11.1	0.9		14.7	1.5	
100		21.0	22.9	23.1			23.1	1.0	4.5
110	11.3	22.2	41.2	28.8	28.5	10.5	26.2	14.5	19.5
120	24.3	23.2	42.2	26.2	40.5	19.5	28.2	29.0	28.0
130	33.4	32.0	59.4	39.0	44.3	27.2	30.2	33.8	30.2
135			90.0			39.9	42.5	40.0	44.5
140	44.8	59.8		50.9	51.9				
150	76.9			62.1			51.5		

Reference (52)

     Table XI indicates that the degree of degradation was
influenced by the molecular structure of the amino acid. At
120°C the rate of destruction of amino acids by class was in
the following order: sulfur-containing, hydroxy>acidic>neutral,
basic,aromatic.

Table XI
Degradation of Amino Compounds After Heating for One
Hour in Presence of Glucose

Class of Amino Compounds	Percent Degradation at °C		
	120	135	150
Neutral			
a- n-Alkyl	20-28	40	45
b- iso-alkyl	-----	42.5	--
Hydroxy	42	90	--
Aromatic	23	--	60
Acidic	36	--	51
Sulfur-containing	41	--	52
Basic	20-29	40-45	--

Reference (52)

Moisture content of the reaction mixture influenced the degradation of amino acids. Rohan and Stewart (52) reported that chocolate precursor aroma extracts when heated in the dry state for one hour at 100°C., lost 30% of the amino acids by degradation. When very lightly moistened the amino acids degradation dropped to 9% under the same reaction conditions. When the reaction mixture was wetted with an equal weight of water, no amino acid degradation was noticed. Cocoa beans moisture content averaged 5 to 6 % which might be sufficient to inhibit browning reaction at lower temperatures, thus in the early stages of roasting the removal of moisture is important.

Roasting cocoa beans results in the production of volatile and non-volatile compounds which contribute to the total flavor complex. 5-Methyl-2-phenyl-2-hexenal, which exhibited a deep bitter persistant cocoa note, was reported in the volatile fraction (53). It was postulated to be the result of aldol condensation of phenylacetaldehyde and isovaleraldehyde with the subsequent loss of water. The two aldehydes were the principal products of Strecker degradation products of phenyla-lanine and leucine, respectively. Non-volatiles contained diketopiperazines (dipeptide anhydride) which interact with theobromine and develop the typical bitterness of cocoa (54). Theobromine has a relatively stable metallic bitterness, but cocoa bitterness is rapidly noticed and disappears quickly. While cocoa bitterness is felt in the whole mouth, theobromine is recognized by the hind part of the tongue. Furthermore, cocoa bitterness is more intense than that of concentrated aqueous solution of theobromine. The following diketopiperazines had been identified as the components responsible for cocoa bitterness:- cyclo(-Pro-Leu-), cyclo(-Val-Phe-), cyclo(-Pro-Phe-), cyclo(-Pro-Gly-), cyclo(-Ala-Val-), cyclo(-Ala-Gly-), cyclo-(Ala-Phe-), cyclo(-Phe-Gly-), cyclo(-Pro-Asn-), and cyclo-(-Asn-Phe-). Those containing phenylalanine exhibited bitterness resembling that of theobromine. Diketopiperazines have stronger bitterness than the corresponding dipeptides or its two individual amino acids. They develop upon heating proteins to temperature above 100°C. Kato et al (55) reported that roasting serine at 280°C , for 30 min under slow nitrogen stream, resulted in the production of 2,5-diketo-3,6-dimethylpiperazine, which upon alkaline hydrolysis produced the dipeptide alanylalanine. A bitter peptide, cyclo(-L-Leu-L-Trp-), was isolated from casein enzymic digest (56). The formation of cyclo(-Pro-Leu-) in aged sake is responsible for its bitterness (57). Recently, five bitter L-proline-containing diketopiperazines were reported in roasted malt (210°C.) used in dark beer brewing. These compounds and their approximate "bitter threshold % values" in aqueous solutions were: cyclo(-L-Phe-L-Pro-),0.1; cyclo((-L-Leu-L-Pro) , 0.05; cyclo(-L-Pro-L-Pro-),0.1; cyclo(-L-Val-L-Pro-),0.1; and cyclo(-L-Ile-L-Pro-),0.05. The authors concluded that these

diketopiperazines did not contribute directly to beer bitterness
and questioned their role in influencing the taste of the product
(58).

More than 300 compounds had been identified in cocoa
volatiles, 10% of which were carbonyl compounds (59,60).
Acetaldehyde, 2-methylpropanal, 3-methylbutanal, 2-methylbutanal,
phenylacetaldhyde and propanal were products of Strecker
degradation of alanine, valine, leucine, isoleucine, phenyl-
acetaldehyde, and α-aminobutyric acid, respectively. Eckey (61)
reported that raw cocoa beans contain about 50-55% fats, which
consisted of palmitic (26.2%), stearic (34.4%), oleic (37.3%),
and linoleic (2.1%) acids. During roasting cocoa beans these
acids were oxidized and the following carbonyl compounds might be
produced:- oleic : 2-propenal, butanal, valeraldehyde, hexanal,
heptanal, octanal, nonanal, decanal, and 2-alkenals of C_8 to C_{11}.
Linoleic : ethanal, propanal, pentanal, hexanal, 2-alkenals of
C_3 to C_{10}, 2,4-alkadienals of C_9 to C_{11}, methyl ethyl ketone
and hexen-1,6-dial. Carbonyl compounds play a major role in
the formation of cocoa flavor components.

Another example of food in which the browning reaction
occurs at near anhydrous condition is coffee. Coffee beans
are usually roasted at temperatures ranging from 180° to 260°C.
for specific period to obtain the desired degree of roasting
(light, medium, and dark). Protein, sucrose, and chlorogenic
acid were the compounds drastically destroyed in coffee beans
upon roasting, Table XII "the data in this table were not
corrected for dry weight loss which varied from 2 to 5%"(62).

Table XII Composition of Green and Roasted Coffee

Constituent	Percent, Dry Basis	
	Green	Roasted
Hemicelluloses	23.0	24.0
Cellulose	12.7	13.2
Lignin	5.6	5.8
Fat	11.4	11.9
Caffeine	1.2	1.3
Sucrose	7.3	0.3
Chlorogenic acid	7.6	3.5
Protein(Based on nonalkaloid nitrogen)	11.6	3.1
Trigonelline	1.1	0.7
Reducing sugars	0.7	0.5
Unknown	14.0	31.7
Total	100.0	100.00
Reference (62)		

The degree of roasting influenced the magnitude of degradation of sucrose, the major sugar present in coffee, Table XIII.

Table XIII
Effect of Roasting On Sucrose Content In Coffee
(Percent Dry Basis)

	Colombian		Santos	
	Sucrose Content	% Loss	Sucrose Content	% Loss
Green	4.59		5.47	
Light Roast	0.45	90.20	0.68	87.57
Medium Roast	0.17	96.30	0.27	95.06
Dark Roast	0.06	98.69	0.10	98.17
Reference (62)				

Feldman et al (62) found no noticeable changes in the contents of the following amino acids in roasted coffee beans proteins: alanine, glutamic, glycine, isoleucine, leucine, phenylalanine, proline, tyrosine, and valine. These findings are in agreement with those reported by Underwood and Deatherage (63). Table XIV showed the degree of destruction of amino acids in coffee bean after roasting. It is quite obvious that the magnitude of nonenzymic browning of amino acids was influenced by its molecular structure and degree of roasting.

Coffee oil contains about 47% linoleic, 8% oleic, 1% hexadecenoic, 32% palmitic, 8% stearic, and 5% behenic and longer chain fatty acids (64). As linoleic acid is the major unsaturated fatty acid in coffee oil, its major oxidation products 2,4-alkadienals and hexen-1,6-dial would play a major role in volatile production. Green coffee beans contain 50 to 60% carbohydrates: 18% nonhydrolyzable cellulose, 13% hydrolyzable cellulose, 13% starches and pectins easily solublized, and 9-12% soluble carbohydrates of which sucrose is the major component. Raffinose and stachyose are the tri- and tetrasaccharides reported in robusta coffee beans. Arabinogalactan and galactomannon are the water-soluble polysaccharides reported in coffee beans (62). The above mentioned carbohydrates, amino acids, lipids along with other flavor precursors produce several hundreds of volatile and nonvolatile compounds through different reactions during roasting. Molecular structures, quantities, and ratios of these compounds influence coffee flavor. The variety of coffee as well as the degree of roasting exert characteristic flavors. The molecular structure of carbonyls influence the type of pryazine formed. While refluxing rhamnose (100g) and ammonia (28%; 40ml) in water (100g) produced methyl- and ethyl-substituted pyrazines, glucose and ammonia reaction resulted in formation of methyl-substituted

Table XIV

Composition of Amino Acids in Green and Roasted Coffee

(After Acid Hydrolysis), %

Amino Acid	Haita			Columbia			Angola Robusta		
	Green	Roast I	Roast II	Green	Roast I	Roast II	Green	Roast I	Roast II
Arginine	4.72	0.00	0.00	3.61	0.00	0.00	2.28	0.00	0.00
Asparagine	10.50	9.07	9.02	10.61	9.53	7.13	9.44	8.94	8.19
Cysteine	3.44	0.38	0.34	2.89	0.76	0.69	3.87	0.14	0.14
Histidine	2.85	1.99	2.17	2.79	2.27	1.61	1.79	2.23	0.85
Lysine	6.19	2.54	2.74	6.81	3.46	2.76	5.36	2.23	2.56
Methionine	2.06	2.32	1.48	1.44	1.08	1.26	1.29	1.68	1.71
Serine	5.60	1.77	1.26	5.88	2.60	0.80	4.97	0.14	0.00
Threonine	3.73	2.43	1.83	3.82	2.71	1.38	3.48	2.37	1.08
Total	39.09	20.50	18.84	37.85	22.41	15.63	32.48	17.73	14.53
Loss %		47.56	51.80		40.79	60.02		45.41	55.26

Reference (62)

pyrazines only (53). The flavors of the products of cysteine-glucose and cysteine-pyruvaldehyde in anhydrous condition at different temperatures 80-190°C. are listed in Table XV (24). Five-mM cysteine+5-mM glucose or pyruvaldehyde reacted at different temperatures for 5 minutes and then evaluated by flavor panel.

Table XV

Flavors Produced by Cysteine-glucose And
Cysteine-pyruvaldehyde at Different Temperatures

Reactants	Flavor Description, at °C.				
	80°	100°	130°	160°	190°
Cysteine & Pyruvalde-hyde	Japanese rice cracker weak.	Sesame, weak	Sesame.	Japanese rice cracker with sesame-like.	Sesame-burnt.
Cysteine & Glucose	no odor	no odor	Japanese rice cracker with seasame-like, sweet.	Japanese rice cracker with sesame-like.	Sweet sesame, burnt.

Reference (24)

Pyruvaldehyde is a liquid at room temperature and boils at 72°C, thus when cysteine-pyruvaldehyde mixture was heated at 80°C, the components are in solution and flavor notes reminiscent of Japanese rice cracker developed. As reaction temperatures increased gradually other flavor notes developed. In the case of cysteine-glucose system, no reaction took place until the reaction temperature reached 130°C. The flavor of cysteine-glucose was comparable to that of cysteine-pyruvaldehde at 160°C, with one exception, the glucose system had a sweet note. As temperature increased the flavor impression of both systems increased in similarity. The volatile compounds produced at 160°C in the presence of pyruvaldehyde were different from those in presence of glucose. While thiazole and thazolines were absent in the volatiles of cysteine-glucose, cysteine-pyruvaldehyde volatiles were devoid of pyridines, picolines and furans (24).
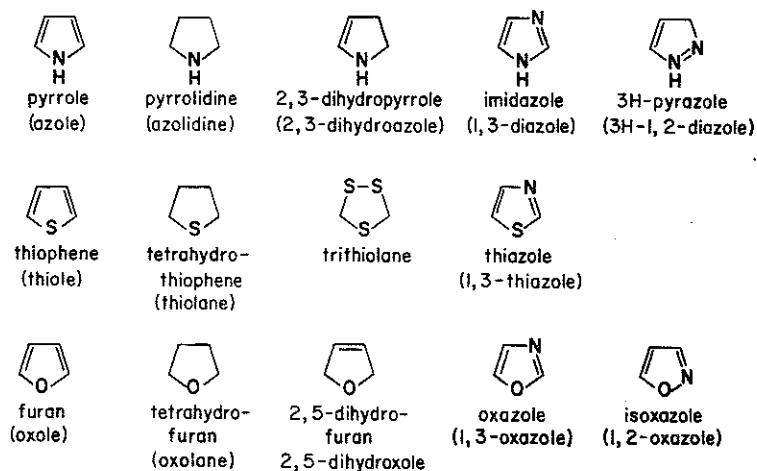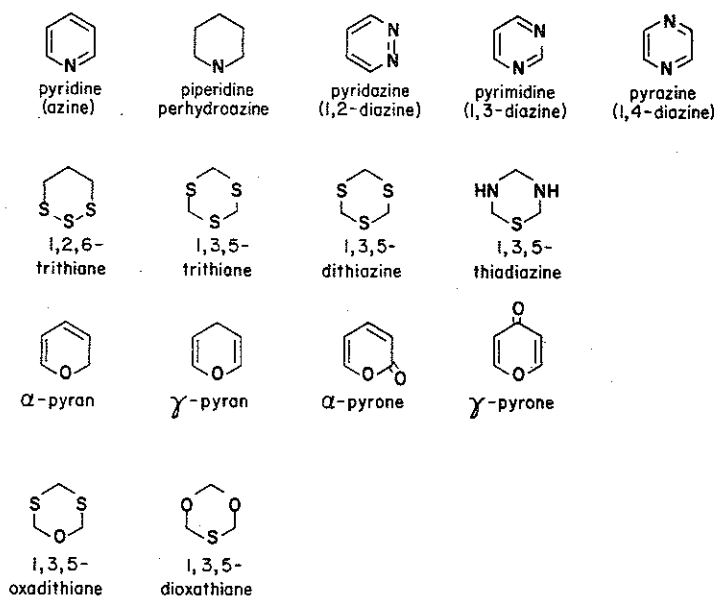
Food flavors consist of numerous compounds, none of which alone is characteristic of specific food. Classes of compounds which emcompass food flavors are:- hydrocarbons (aliphatic, alicyclic, aromatic); carbonyls (aldehydes, ketones); carboxylic acids, esters, imides, anhydrides; alcohols, phenols, ethers; alkylamines, alkylimines; aliphatic sulfur compounds (thiols, mono-, di- and tri-sulfides); nitrogen heterocyclics (pyrroles, pyrazines, pyridines); sulfur heterocylics (thiophenes, thiazoles, trithiolane, thialidine); and oxygen-heterocyclics (lactone, pyrone, furan). Discussion will be limited to striking developments in heterocyclics.

Heterocyclic Compounds

During browning reaction in foods, heterocyclic compounds of known five- and six-membered ring systems containing one or more atoms than carbon as ring members, are produced. These compounds encompass several classes of compounds that exhibit desirable characteristic organoleptic notes, i.e. toasted, bread-like, roasted, brothy, mushroom-like, nutty, ... etc., or undesirable notes, e.g. peppery ammoniacal, obnoxious, ... etc. The nomenclatures and the molecular formulas of heterocyclic compounds that most frequently encountered in food volatiles are given in Figures 1 and 2.

Nitrogen-heterocyclic

Pyrrole and pyrrole derivatives. The chemical and biological value of pyrrole and its derivatives cannot be overemphasized, natural pigments, heme, chlorophyll, bile pigments and enzymes like cytochromes, contain pyrrole nucleus. Also, many alkaloids, proline and hydroxyproline contain the reduced pyrrole ring (pyrrolidine). Pyrrole and its derivatives are found among the products of the browning reaction products in processed foods. Alkylpyrroles have intense petroleum-like odor, but they give sweet, slightly burnt aroma on extreme dilution. On the other hand acylpyrroles have characteristic sweet smoky, and a little medicine-like odor (65). Although alkyl- and acyl- pyrroles do not exhibit favorable aroma like the desirable roasty aroma of pyrazines, they may play an important role in the characteristic roasty flavor of processed foods. In anhydrous condition, N-acetonylpyrrole, which had a bread-like aroma was isolated from the roasting products of proline-glucose, hydroxyproline-glucose, and pyrrolidine-pyruvaldehyde (66). 1-Pyrroline which exhibited an amine like or corn-like odor was the product of Strecker degradation of proline-, and ornithione-sugar or- polycarbonyl reagents in aqueous solutions (67). 2-Pyrrolealdehyde, 2-acetylpyrrole, 2-propionylpyrrole, N-methyl-2-pyrrolealdehyde, N-methyl-2-acetyl pyrrole, 5-methyl-2-pyrrolealdehyde, N-methyl-5-methyl-2-pyrrole-

pyrrole
(azole)

pyrrolidine
(azolidine)

2,3-dihydropyrrole
(2,3-dihydroazole)

imidazole
(1,3-diazole)

3H-pyrazole
(3H-1,2-diazole)

thiophene
(thiole)

tetrahydro-
thiophene
(thiolane)

trithiolane

thiazole
(1,3-thiazole)

furan
(oxole)

tetrahydro-
furan
(oxolane)

2,5-dihydro-
furan
2,5-dihydroxole

oxazole
(1,3-oxazole)

isoxazole
(1,2-oxazole)

Figure 1.   Five-membered ring heterocyclics

pyridine
(azine)

piperidine
perhydroazine

pyridazine
(1,2-diazine)

pyrimidine
(1,3-diazine)

pyrazine
(1,4-diazine)

1,2,6-
trithiane

1,3,5-
trithiane

1,3,5-
dithiazine

1,3,5-
thiadiazine

α-pyran

γ-pyran

α-pyrone

γ-pyrone

1,3,5-
oxadithiane

1,3,5-
dioxathiane

Figure 2.   Six-membered ring heterocyclics

aldehyde were identified in the pyrrolic fraction of coffee
volatile constituents (68, 69). N- ethylpyrrole-2-aldehyde and
5-methylpyrrole-2-aldehyde are two of the eighteen compounds re-
ported in stored dehydrated orange juice crystals due to nonenzy-
mic browning (70). The type of pyrrole derivatives produced de-
pended on reaction temperature, its duration, its condition, i.e.,
anhydrous, aqueous, or alcoholic; pH of the media, and molecular
structure of reactants. While, N-alkylpyrrole-2-aldehydes were
produced upon heating D-xylose and alkylamine or amino acid in
neutral aqueous or methanolic solutions at 55⟨100°C; the corre-
sponding 5-methyl derivatives of N-substituted pyrrole-2-aldehydes
were formed in the presence of L-rhamnose (71, 72). Odor of the
products were: N-methylpyrrole-2-aldehyde (formed from D-xylose
and methylamine) cinnamonaldehyde-like, N-n butylpyrrole-2-alde-
hyde (a product of butylamine-xylose); and 1-n-butyl-5-methyl-
pyrrole-2-aldehyde (rhamnose and butylamine interactions product)
xylene-like. 2-Formylpyrrol-1-yl-alkyl acids were isolated from
the products of the browning reaction of xylose and alkylamines
or amino acids in aqueous solutions (73). N-substituted-5-(hydro-
xymethyl)-pyrrole-2-aldehydes were formed from the reaction of the
aldohexose "glucose" and alkylamines or amino acids containing
primary amino group at 70 to 100°C, in neutralized aqueous,
methanolic or ethanolic solutions. The resulting compounds were
considerably unstable and had no odor in the pure state but devel-
oped roasted aroma with browning (74). Upon roasting glucose and
several alkyl-n-amino acid (glycine, α-alanine, α-amino-n-butyric,
valine, leucine, α-amino-n-caproic) at 200-250°C in two components
systems; 2-5'-hydroxy-methyl-2'-formylpyrrol-1'-yl) alkanoic acid
lactones were formed as the main volatile products (75). The
aroma description of the prepared lactone derivatives were: pro-
pionic acid lactone (from α-alanine and glucose) caramel and a
little scorching; isobutyric acid lactone (α-amino-n-butyric and
glucose) maple and strong sweet; isovaleric acid lactone (valine
and glucose) and isocarproic acid lactone (leucine and glucose)
miso, soy sauce and a chocolate-like. The yield of propionic acid
lactone after heating an equimolar mixture of 0.01 mole of glucose
and α-alanine at 150, 200, and 250°C were:

Temperature, °C	Heating period, min.	Yield, unmoles
250	1	42
250	5	3 - 4
200	3	50
200	5	6
150	5	16

It is quite obvious from the above data that the propionic acid
lactone disappeared during the reaction for longer periods and at
higher temperatures. 2-(5'-hydroxymmethyl-2'-formylpyrrol-1'-yl)
-3-methylbutanoate, and 2'-(5'-hydroxymethyl-2'-formyl-

pyrrol-1'-yl)-3-methylbutanoic acid lactone were identified in the
products of the browning reaction of glucose and valine in aqueous
solution at 65°C for three weeks (76). Reducing disaccharides
(lactose, maltose and melibiose) reacted with alkylamine in
aqueous solutions of pH 6.5, to form 1-alkyl-5-hydroxymethylpyr-
role-2-aldehyde (77). N-Alkyl-2-acylpyrroles and aliphatic aldi-
mines were the products of the reaction between furfural and its
homologs with α-amino acids (78). Reactions of furfural and 2-
acetylfuran with glycine and valine produced a small amount of the
corresponding acylalkylpyrroles which had pleasant aromas remini-
scent of benzaldehyde. The resulting considerable amount of ali-
phatic aldimines from the reaction of furfural with valine and
leucine possessed a strong odor from biting and unpleasant to mild
and food-like. Nine alkylpyrroles, three acylpyrroles, three
alkylpyrrole-2-aldehydes, three furfurylpyrrole, eight alkylpyra-
zines, and one oxazoline were identified in the volatile flavorous
products of roasting DL-alanine and glucose at 250°C for one hour
in nitrogen atmosphere (79). Many of the compounds identified in
the reaction products of model systems had been isolated from
roasted and cooked foods. For example, pyrrole, 1-methylpyrrole,
2-methylpyrrole, 1-formylpyrrole, 2-formylpyrrole, 1-formyl-2-
methylpyrrole, 2-formyl-1-methylpyrrole, 2-formyl-1-methylpyrrole,
2-formyl-5-methylpyrrole, 2-formyl-1-ethylpyrrole, 1-acetylpyr-
role, 2-acetylpyrrole, 1-furfurylpyrrole, 2-propionylpyrrole, 2-
formyl-1-furfurylpyrrole were reported in roasted peanut (80).
Roasted filberts volatiles contained 1-methylpyrrole, 2-pentylpyr-
role, 2-isobutylpyrrole, and 2-penrylpyrridine (81).

   Pyridine and its derivatives. The most unique pyridine deri-
vative isolated from processed food is 1,4,5,6-tetrahydro-2-ace-
topyridine. This compound was prepared by roasting proline and
dihydroxyacetone at 92°C in presence of sodium bisulfate, and ex-
hibited a strong odor reminiscent of freshly backed soda crackers
(82). 2-Ethylpyridine and 2-pentylpyridine were reported in
volatile flavor components of shallow fried (83). Pyridine, 2-
methylpyridine, 3-methylpyridine, 2-ethylpyridine, 3-ethylpyri-
dine, 5-ethyl-2-methylpyridine, 2-butylpyridine, 2-acetylpyridine,
2-pentylpyridine, 2-hexylpyridine, 3-pentylpyridine, 5-methyl-2-
pentylpyridine, and 5-ethyl-2-pentylpyridine were identified in
the volatiles of roasted lamb fat (84). 2,5-Dimethylpyridine and
3,5-dimethylpyridine were tentatively identified in roasted lamb
fat volatiles. The odor threshold of 2-pentylpyridine was 0.5-0.7
parts per 10^9 parts of water. The dilute solution of 2-pentylpy-
ridine has a fatty or tallow-like odor. The authors attribute the
unacceptance of lamb by some consumers to the high content of
alkylpyridines in roasted lamb. While pyridine derivatives have
burnt, heavy fruity odors (85); pyridine has a disagreeable char-
acterisitic odor and sharp taste; and piperidine has a peppery
ammoniacal odor (86). Pyridine, α-picoline (2-methylpyridine),
β-picoline (4-methylpyridine), and 4-ethylpyridine were identified

in coffee aroma (87).

Pyrazines. In the thirties, the attention on pyrazines was
focused on its industrial role in dyes, photographic emulsions and
chemotherapy. Its importance in life processes was indicated in
its derivative, vitamin B_2 (riboflavin, 6,7-dimethyl-9-(1'-D-
ribityl isoalloxazine). Later, in the midsixties, it was identified
in foods and its contributions to the unique flavor and aroma of
raw and processed foods attracted the attention of flavor chemists.
Pyrazine derivatives contribute to the roasting, toasting, nutty,
chocolaty, coffee, earthy, caramel, maple-like, bread-like,
and bell pepper notes in foods. The reader is referred to the
reviews on Krems and Spoerri (88) on the chemistry of pyrazines,
and the review of pyrazines in foods by Maga and Sizer (89, 90).
Table XVI summaries sensory description and threshold of selected
pyrazines.

Oxygen Heterocyclics. During heat processing, sugars degrade
to aldehydes and ketones which might react with amino compounds
forming caramelized sugar flavors. Cyclic diketones, pyrones, and
furan derivatives are examples of the products of this reaction.
Table XVII gives the organoleptic description of selected com-
pounds. 4-Hydroxy-2,5-dimethyl(2H)-furanone has intense fragrant
caramel note described as burnt sweet taste (70), burnt pineapple
(101), beef broth (100), strawberry preserve (103), nutty sweet
aroma of almonds (104), and major contributor to sponge cake
flavor (105). Seven terms were used to describe the organoleptic
note of one compound. The question arises, what was the concen-
tration and media used for evaluation? Change in concentration
alone can be quite sufficient to alter the character of the flavor
or odor note. For example, trimethylamine-air mixtures only smell
fishy over a narrow range of dilutions (1:1,500-1:8,000), with a
maximum at about (1:6,000), also ammonia at a dilution of about
(1:2,000) smells fishy (106). Hodge and Moser (107) reported that
inspite of the fact that the aromas of pure maltol, ethyl maltol,
isomaltol, and 4-hydroxy-2,5-dimethyl-3(2H)-furanone vary signifi-
cantly from each other, panelists description was caramel or burnt
sugar. The fruity caramel aroma of isomaltol is weaker than that
of 4-hydroxy-2,5-dimethyl-3(2H)-furanone (108). Our sensory vo-
cabulary should be adequate to express the impact of flavor, odor,
taste notes components. This could be achieved by the participa-
tion of food chemist, organic chemist, sensory analyst and flavor-
ist. Soy sauce (Shoyu) contains tautomers 4-hydroxy-2-ethyl-5-
ethyl-3(2H)-furanone and 4-hydroxy-5-ethyl-2-methyl-3(2H)-furanone
(about 3:2 ratio) which has sweet odor similar to that of short
cake (109). The same tautomers were synthesized and described as
possessing the flavor of cooked fruits (103). Maltol, isomaltol
and 2-methyl-5-hydroxy-6-ethyl-α-pyrone are contributors to the
characteristic aroma of molasses (110).

Table XVI

Pyrazines, Sensory Description and Odor Threshold

Pyrazine	Sensory Description	Odor Threshold ppm		
		Water	Mineral Oil	Vegetable Oil
2-Methyl-	deep bitter persistent cocoa notes (5)	105 (91) 60 (92)	27 (91)	
2,3-Dimethyl-		2.5 (92)	—	
2,5-Dimethyl-	earthy raw potato (3)	3.5 (91) 1.8 (92)	7 (91)	
2,6-Dimethyl	sweet fried odor (2)	54 (91) 1.5 (92)	8 (91)	2.6 (91)
2,3,5-Tri-methyl		9 (91)	27 (91)	
2,3,5,6-Tetra-methyl		10 (91)	38 (91)	
2-Ethyl		60 (92) 22 (91)	17 (91)	
2-Ethyl-3-methyl-		0.13 (92)		0.32 (92)
2-Ethyl-5-methyl		0.10 (92)		
2-Ethyl-3,6-dimethyl-		0.0004 (92)	—	0.024 (92)

Table XVI

Pyrazines, Sensory Description and Odor Threshold (Cont.)

Pyrazine	Sensory Description	Water	Odor Threshold ppm Mineral Oil	Vegetable Oil
2,6-dimethoxy-3-isopropyl-5-methyl	nutty with green-like bell-pepper, woody notes (96)			
2,5-dimethoxy-3-isopropyl-6-methyl	nutty notes, green (bell-pepper-like) (96)			
5-methyl 5H-6,7-dihydrocyclopenta	peanuts (53)			
5-methyl-2H-3,4,5,7-retrahydrocyclopenta	roasted nuts, burnt (53)			
2-acetyl-	breadcrust, nutty (96)			
2-methoxy-3-acetyl-	weak breadcrust, nutty notes (96)			
2-methylamino-3-methyl	roasted peanuts, green cocoa notes (96)			
2-dimethylamino-3-methyl	Peanut-like more green and less cocoa notes (96)			
2-dimethylamino-6-methyl	peanut-like, no cocoa notes reminiscent of burnt coffee (96)			

Table XVI

Pyrazines, Sensory Description and Odor Threshold (Cont.)

Pyrazine	Sensory Description	Water	Mineral Oil	Vegetable Oil
2,5-diethyl-				
2,6-diethyl-		0.02 (92)		0.27 (92)
5-Ethyl-2,3-dimethyl	chocolate sweet (93)	0.006 (92)		
2,5-Dimethyl-3-ethyl		43 (91)	24 (91)	
2,6-Dimethyl-3-ethyl		15 (91)	24 (91)	
Methyl isoamyl-	green cocoa note (95)			
Ethyl isoamyl-	green cocoa note (95)			
2-Methylamine-3-methyl-	cocoa notes, roasted peanuts, green (96)			
2-Dimethylamine-3-ethyl	less cocoa note (96)			
2-Methyl-3-methoxy-	roasted peanut (91)			
	nutty earthy (97)			
2-Methylthio-3-methyl-	nutty cracker (97)			

References (53, 91-97).

Table XVII

Oxygen Heterocyclic Compounds

Compound	Sensory Description
Furan	Spicy, smoky, slightly cinnamon-like odor (98). Sweet bread-like, caramel-like taste (98).
Furfuryl alcohol	Coconut (99).
5-methyl-2-furfural	Sharp grape (98).
Maltol (3-hydroxy-2-methyl-pyrone)	Pleasing strong fruitsy fresh bread (99).
Isomaltol	Fruity caramel, fresh bread odor, overtone medicinal grassy (99).
N-Furfuryl pyrrole	Green hay-like aroma (98).
4-hydroxy-5-methyl-3(2H)-Furanone	Beef broth (100) burning sweet taste (70), burnt pineapple (101).
2,5-Dimethyl-4-hydroxy-3(2H)-Furanone	Odor of roasted chicory roots (102).

References (98 - 102).

Sulfur Heterocyclics. Sulfur containing compounds (thiols, thiophenes, thiazoles, ... etc.) play a major role in the flavor of raw and processed foods. These compounds have characteristic flavor notes and the flavor thresholds are mostly low. Several reviews (111, 112, 113) demonstrate the important role of sulfur compounds in food flavors. Organoleptic properties of these compounds may be pleasant, strong nut-like odor of 4-methyl-5-vinylthiazole which is present in cocoa (114); objectionable pyridine-like odor of thiazole (115); quinoline-like odor of benzothiazole (116); strong tomato leaf-like odor of isobutylthiazole (117); and bread crust flavor of acetyl-2-thiazoline (118). A mixture of oxazoles, thiazoles, thiazolines, imidazoles, trithiolanes and

dithianes which had a meaty flavor was obtained from a model system consisting of α-dicarbonyls, ethanal, hydrogen sulfide and ammonia (119). Unsaturated aldehydes react with hydrogen sulfide and thiols to give mainly addition products to the carbon-carbon double bond (120). The nomenclature of the resulting compounds and their organoleptic descriptions are given in Table XVIII. Thiols, thiophenes, thiazoles, sulfides and furans were identified in the volatiles of heating glucose, hydrogen sulfide, and ammonia at 100°C for two hours (121). These volatiles gave a roast beef-like aroma. Complex mixtures of mercapto-substituted furans and thiophene derivatives, which were reminiscent of roast meat were produced upon heating 4-hydroxy-5 methyl-3(2H)-furanone and its thio analog with hydrogen sulfide (122).

Lipid Browning.

Lipid browning reactions of the Maillard type between carbonyl groups (provided by sugars or sugar degradation products and those resulting from unsaturated fatty acids oxidation) and the free amino groups present in phospholipids have been recognized as potent causes of undesirable flavor, color and texture changes in dehydrated foods (123). Phosphatidyl ethanolamine, phosphatidyl serine, ethanolamine and serine plasmalogens contain free amino groups which can undergo lipid browning reactions. Phospolipids are usually rich in highly unsaturated fatty acids in comparison with neutral lipids, thus they are good sources of carbonyls. Also, the primary amine moities of polar lipids catalyze the aldol condensation of C_{14}-C_{18} aldehydes resulting from plasmalogen hydrolysis, thus forming α,β-unsaturated aldehydes (124). Phosphatidyl ethanolamine reacted with propanal and n-hexanal forming phosphatidyl 1-(2-hydroxyethyl)-2-ethyl-3,5-dimethyl pyridinium, and phosphatidyl-1-(2-hydroxyethyl)-2-hexyl-3,5-dipentyl pyridinium, respectively (125). The peridinium ring is formed by the reaction between one mole of amino-N of phosphatidyl ethanolamine and three moles of n-alkanals. The same reaction took place in the synthesis of substituted pyridines by condensation of carbonyl compounds with ammonia (126, 127).

Abstract

In processed foods, non-enzymic browning reaction is the major source of its desirable flavors. Flavors of the products of this reaction depend upon: the molecular structure of nitrogenous compounds (amines, amino acids, peptides, glycopeptides, proteins, ... etc.); aldoses, ketoses, non-reducing, deoxy sugars, sugar acids, ... etc.); heating temperature; duration of the reaction; initial hydrogen ion concentration, moisture content, and the media of the reaction (alcoholic, aqueous, or anhydrous). The ratio of the nitrogenous compound to sugar or carbonyl compound has great effect on the flavor notes. Comparison betwen browning

Table XVIII

Flavor of Products of the Addition Between Unsaturated Carbonyls and Methanethiol

Carbonyl Added	Addition Product	Flavor Impression	Water	Paraffin Oil
2-Butenal	3-methyl thiobutanal	Cheese-like (Brite)	0.5	0.5
2-Hexenal	3-Methyl thiohexanal	Cabbage (Rubbery)	5	50
2-Hebtenal	3-Methyl thioheptanal	Unripe tomato	5	80
2-Nonenal	3-Methyl thiononal	Bast-like, slightly floral	3	20
1-Octene-3-one	1-Methyl thiooctan-3-one	Radish-like		

Reference (120).

reaction products and rate of degradation of reactants under anhydrous condition, aqueous and alcoholic media was discussed. Flavor notes of products of amino compounds-sugars reaction were reviewed with emphasis on amino-ribose system. Meat-like flavor was imparted by browning reaction products of carnosine-, citrulline-, histidine-, glutamic-, 2-pyrrolidone-5-carboxylic-, methionine-, cysteine-, cysteic-, and taurine-ribose. Recent advancements in nitrogen-, oxygen- and sulfur hetercyclics and lipid browning were presented.

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